

Zr₅Ir₃ with a Deformation Superstructure of the Mn₅Si₃ Structure

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Abstract. $M_r = 1032.7$, $hP48$, $P6_122$, $a = 7.9306$ (7), $c = 17.010$ (2) Å, $V = 926.5$ (2) Å³, $Z = 6$, $D_x = 11.10$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 75.8$ mm⁻¹, $F(000) = 2586$, $T = 293$ K, $wR = 0.046$ for 795 independent reflections. Hf₅Ir₃ crystallizes with the same structure type. The Zr₅Ir₃ structure is a deformation superstructure of the hexagonal Mn₅Si₃ structure where $c = 3c[\text{Mn}_5\text{Si}_3]$. The chains of majority atoms along $\frac{1}{3}\frac{2}{3}z$ and $\frac{2}{3}\frac{1}{3}z$, where very short distances occur in the parent structure type, are no longer straight but undulated. At the same time the coordination number of two thirds of the minority atoms is reduced from nine to eight.

Introduction. The Mn₅Si₃ structure type is well known and found with a large number of aluminides, gallides, silicides, germanides, etc. The octahedral interstices on the c axis are sometimes partially or completely filled (Mo₅Si₃C_{1-x} and Ti₅Ga₄ type), phases with these structures being called Nowotny phases. When Biswas & Schubert (1967) reported that Zr₅Ir₃, Hf₅Ir₃ and Zr₅Pt₃ crystallize with the Mn₅Si₃ type, it was the first time that this type was observed with compounds where both components are transition elements. Since then the same type has also been found with a series of rare-earth-metal-transition-metal alloys (Raman & Ghassem, 1973; Iandelli & Palenzona, 1975; Le Roy, Moreau, Paccard & Parthé, 1978; Iandelli & Palenzona, 1982; Le Roy, Moreau & Paccard, 1982). The axial ratios c/a for these rare-earth compounds are rather high, as compared with those measured for the transition-metal silicides and homologues, whereas those calculated for the isotypic Zr and Hf alloys with Ir and Pt are in comparison lower. The existence of a compound forming peritectically at the approximate composition Zr₅Ir₃ was confirmed by the reinvestigation of the Zr–Ir phase diagram (Eremenko, Semenova & Shtepa, 1980). In the Zr–Ir as well as the Hf–Ir system, Schubert and coworkers (Raman & Schubert, 1964; Biswas & Schubert, 1967) observed two phases with similar structures in a narrow composition range. In addition to the Mn₅Si₃-type phases – observed slightly off stoichiometry and therefore called Zr_{<5}Ir₃, later on – they found indications of the existence of a superstructure at the stoichiometric composition. The

phase diagram of the Hf–Ir system was studied by Copeland & Goodrich (1969) who reported an Hf₅Ir₃ compound of unknown structure with a hexagonal unit cell of $a = 7.863$ and $c = 16.89$ Å, i.e. with a c axis about three times as long as expected for the Mn₅Si₃ type.

Dr R. M. Waterstrat prepared a sample of Zr₅Ir₃ in order to see if a new structure type existed at this composition. It then seemed of interest to us to determine the atom arrangement of this superstructure and to look for the differences with the Mn₅Si₃ type.

Experimental. A sample of nominal composition Zr₅Ir₃, annealed at 1773 K for 3 h, was kindly provided by Dr R. M. Waterstrat. The powder diagram shows similarities with the simulated powder diagram calculated for the type Mn₅Si₃ using the program *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977), but contains additional lines. Single crystal of irregular shape (mean radius 15 µm); Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell parameters refined from 2θ values of 20 reflections (Mo $K\alpha_1$, $\lambda = 0.70930$ Å; $36 \leq 2\theta \leq 50^\circ$) using the program *FINAX* (Hovestreydt, 1983). Laue symmetry $6/mmm$; systematic absences $00l \ l \neq 6n$, leading to possible space groups $P6_122$ and $P6_522$. 1222 reflections collected out to $\sin\theta/\lambda = 0.70$ Å⁻¹ ($0 \leq h, k \leq 11$, $0 \leq l \leq 23$ and all antireflections) in ω - 2θ scan mode, yielding 894 independent reflections ($R_{\text{int}} = 0.033$), of which 587 considered significant [$|I| \geq 3\sigma(I)$]. Standard reflections $3\bar{1}3$ and $31\bar{3}$ (max. intensity variation $\pm 4.9\%$); spherical absorption correction ($\mu R = 1.137$; $4.429 \leq A^* \leq 4.929$). Positions of 18 Ir and six Zr atoms found by direct methods, program *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), further starting positions for 24 Zr atoms calculated supposing an atom arrangement as in the Mn₅Si₃ type, $P6_122$ (or $P6_522$) being a subgroup of index 6 of $P6_3/mcm$. Full-matrix refinement in $P6_122$ using $|F|$ values of 795 independent reflections (including 208 ‘less-thans’ calculated greater than observed), of which 551 were superstructure reflections. Ten positional parameters and six isotropic displacement parameters, listed in Table 1,

Table 1. Atomic coordinates (and isotropic displacement parameters) for Zr₅Ir₃ with a superstructure of the Mn₅Si₃ type, *hP48*, *P6₁22*, compared with the atomic coordinates for Ho₅Rh₃, with the Mn₅Si₃ parent type, referred to a triple cell (*c'* = 3*c*) with space group *P6₁22* and referred to the conventional unit cell with space group *P6₃/mcm*

The temperature factor is expressed as $T = \exp[-2\pi^2 U(2\sin\theta/\lambda)^2]$. E.s.d.'s are given in parentheses.

Zr ₅ Ir ₃ , superstructure						Ho ₅ Rh ₃ , Mn ₅ Si ₃ type									
<i>P6₁22</i>						<i>P6₁22</i>									
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ² × 100)		<i>x</i>	<i>y</i>	<i>z</i>	<i>P6₃/mcm</i>						
Zr(1A)	12(c)	0.2384 (5)	0.0062 (5)	0.3396 (2)	0.91 (6)	Ho(1A)	12(c)	0.2457	0	$\frac{1}{3}$	Ho(1)	6(g)	0.2457	0	$\frac{1}{4}$
Zr(1B)	6(a)	0.2480 (6)	0	0	0.97 (9)	Ho(1B)	6(a)	0.2457	0	0					
Zr(2A)	6(b)	0.3710 (4)	2 <i>x</i>	$\frac{1}{4}$	0.84 (9)	Ho(2A)	6(b)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	Ho(2)	4(d)	$\frac{1}{3}$	$\frac{2}{3}$	0
Zr(2B)	6(b)	0.6557 (3)	2 <i>x</i>	$\frac{1}{4}$	0.72 (9)	Ho(2B)	6(b)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$					
Ir(A)	12(c)	0.4137 (2)	0.0187 (2)	0.1444 (1)	0.91 (3)	Rh(A)	12(c)	0.401	0	$\frac{1}{6}$	Rh	6(g)	0.599	0	$\frac{1}{4}$
Ir(B)	6(a)	0.6111 (2)	0	0	0.75 (4)	Rh(B)	6(a)	0.599	0	0					

one scale factor, one absolute structure parameter $x = 0.39$ (5) (Flack, 1983; Bernardinelli & Flack, 1985), indicating a mixture of microdomains oriented so that their helicoidal axes are parallel but of opposite sense, and one isotropic secondary extinction parameter $g = 4.1$ (1) × 10⁻⁵ (mosaic spread, Gaussian distribution) refined to a final $wR = 0.046$ [$w = 1/\sigma^2(|F_{rel}|)$]; $wR(l \neq 3n) = 0.052$; $S = 1.66$; shift/e.s.d. in last cycle ≤ 0.0002; max. (min.) height of final residual electron density map = 5.0 (-8.7) e Å⁻³. * Atomic scattering factors for neutral atoms, f' and f'' from *International Tables for X-ray Crystallography* (1974); programs used for data reduction and structure refinement from *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

The isotopy of Hf₅Ir₃, $a = 7.863$, $c = 16.89$ Å, can be assumed by comparing the list of intensities measured by Copeland & Goodrich (1969) with the simulated powder pattern calculated with the program *LAZY PULVERIX* (Yvon *et al.*, 1977).

Discussion. The Mn₅Si₃ structure is built up of three kinds of crystallographically different atoms. The Mn(1) atoms form columns of octahedra linked by common faces along the *c* axis while the Mn(2) atoms are arranged in straight chains along $\frac{12}{33}z$ and $\frac{21}{33}z$ and the Si atoms surround octahedrally the Mn(2) atoms, forming similar columns of face-sharing octahedra parallel to the *c* axis. The atomic coordinates refined for the superstructure found with Zr₅Ir₃, *hP48*, *P6₁22*, are compared in Table 1 with those refined for Ho₅Rh₃ with the Mn₅Si₃ type (Le Roy *et al.*, 1982). In the central column the coordinates of Ho₅Rh₃ are referred to a triple unit cell, shifted in the *z* direction, and in the column to the right to the conventional unit cell. The 18

* A list of structure factors, arranged in a standard crystallographic data file (Brown, 1985), has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42932 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atoms arising from the sixfold Ho(1) and Rh sets are each divided into two sets of multiplicity 12 and six, while the 12 atoms from the fourfold Ho(2) set are divided into two sets of multiplicity six. It can be seen from Table 1 that the major differences between the superstructure and the parent structure are to be found at the *x* coordinate of Zr(2A) and the *z* coordinate of Ir(A). The deformation of the Mn₅Si₃ type as it occurs in a slab between $z \simeq \frac{5}{6}$ and $z \simeq 1$ in the superstructure, is shown schematically in Fig. 1(a): one Zr atom [Zr(2A)] moves away from the axis at $\frac{12}{33}z$ towards two Ir atoms [Ir(A)] which move apart in the *c* direction. The 6₁ axis at 00*z* describes the repetition of this combined movement throughout the structure. Fig. 1(b) shows a projection of the real superstructure along [001]. The chains of atoms along $\frac{12}{33}z$ and $\frac{21}{33}z$ are now undulated, every second atom being displaced by 0.52 Å out from the axis. Fig. 2 shows the superstructure in a partial projection along [110] emphasizing the columns of empty Zr octahedra along 00*z* and the columns of Ir octahedra centred by the Zr(2A) and Zr(2B) atoms. The Ir octahedra are strongly distorted, the Ir(A) atoms being shifted out of the planes at $xy\frac{2}{6}$.

Other superstructures of the Mn₅Si₃ type have been mentioned in the literature. Ca₅Pb₃ crystallizes with a hexagonal superstructure also with 48 atoms per unit cell, but where the new *a* axis is related to the unit-cell vectors of the Mn₅Si₃ type according to $a' = 2a_1 + a_2$ [Mn₅Si₃] and the *c* axis is the same (Helleis, Kandler, Leicht, Quiring & Wölfel, 1963). In this structure type, space group *P6₃mc*, the columns of majority atoms along $\frac{12}{33}z$ (referred to the original Mn₅Si₃ cell) remain straight but there is a displacement of the atoms forming the octahedra along 00*z*, in and perpendicular to the (001) plane. The high-temperature form of Eu₅As₃ crystallizes with what is called a disordered Ca₅Pb₃ type where several, partially occupied sets with different *z* values have been refined (Wang, Calvert, Gabe & Taylor, 1978). The low-temperature form crystallizes with the simple Mn₅Si₃ type. Extra X-ray diffraction spots on Weissenberg

films have also been observed for some Re_5Ir_3 compounds (Le Roy *et al.*, 1982). All spots could be indexed by using a cell where $a' = 2a_1 + a_2[\text{Mn}_5\text{Si}_3]$ and $c' = 3c[\text{Mn}_5\text{Si}_3]$, but the superstructure could not be solved.

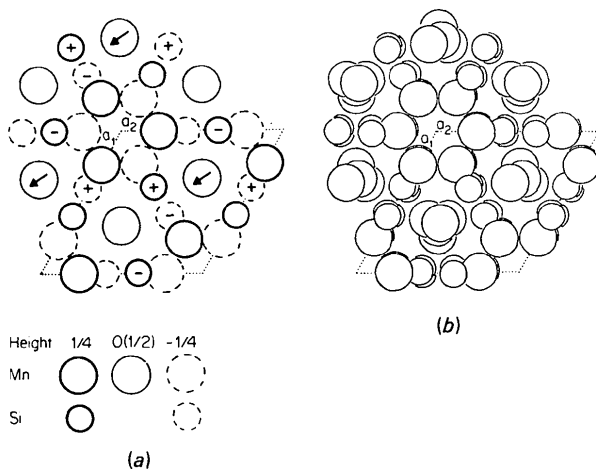


Fig. 1. (a) Projection of the Mn_5Si_3 parent structure. Arrows and plus and minus signs indicate the directions of the displacements, observed in a layer of the Zr_5Ir_3 -type superstructure between $z \approx \frac{1}{2}$ and $z \approx 1$, from the atom sites of the parent structure. (b) Projection along $[001]$ of the real superstructure found with Zr_5Ir_3 . Large circles indicate Zr atoms, smaller circles Ir atoms.

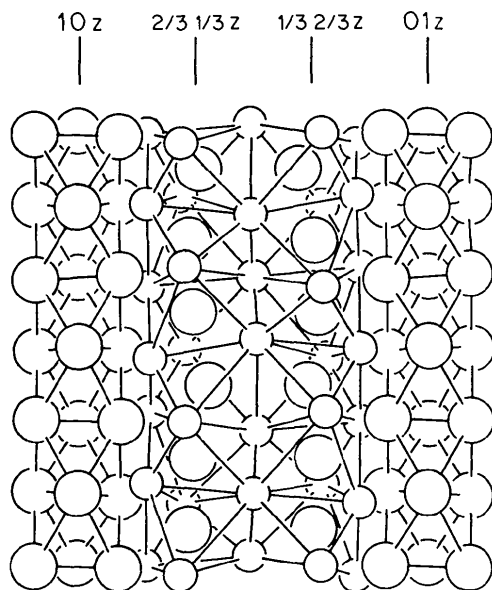


Fig. 2. Partial projection of the Zr_5Ir_3 superstructure along $[110]$ showing the columns of empty, face-sharing Zr octahedra along $10z$ and $01z$ and the columns of, equally face-sharing, Ir octahedra, centred by $\text{Zr}(2A)$ and $\text{Zr}(2B)$ atoms, along $\frac{2}{3}z$ and $\frac{1}{3}z$.

The nearest neighbours at distances (d) shorter than 4 \AA for all atom sites in Zr_5Ir_3 , $hP48$, are listed in Table 2 and compared with those calculated for $\text{Zr}_{<5}\text{Ir}_3$ with the Mn_5Si_3 parent structure type, $hP16$, $a = 8.025$, $c = 5.488 \text{ \AA}$ (Biswas & Schubert, 1967), using the coordinates refined for Ho_5Rh_3 (Le Roy *et al.*, 1982). The relative contractions of the atoms, $\Delta = (d - \sum r) / \sum r$, have also been calculated, using radii (r) for 12-coordinated atoms (Teatum, Gschneidner & Waber, 1960), and expressed in per cent. It is a characteristic of the Mn_5Si_3 parent structure type that the distances between the atoms forming the chains along $\frac{1}{3}z$ or $\frac{2}{3}z$ are short. In $\text{Zr}_{<5}\text{Ir}_3$ with the Mn_5Si_3 parent structure type these distances are indeed very short (2.744 \AA , $\Delta = -14.4\%$), while in the superstructure Zr_5Ir_3 , where these columns are no longer straight but undulated, the corresponding distances are longer [$\text{Zr}(2A) - \text{Zr}(2B) = 2.899 (1) \text{ \AA}$, $\Delta = -9.5\%$]. The comparable value of $2.904 (3) \text{ \AA}$ is also found as the shortest distance between Zr atoms in Zr_3Ir with the $\alpha\text{-V}_3\text{S}$ type (Cenzual & Parthé, 1985). In contrast, slightly shorter distances are achieved between Zr and Ir atoms in the superstructure. Except for the relative displacement of the $\text{Zr}(2A)$ [or $\text{Zr}(2B)$] atom the coordination numbers of the $\text{Zr}(2A)$ and $\text{Zr}(2B)$ sites do not differ much from that observed for $\text{Zr}(2)$ in the parent structure, even if the Ir octahedra are strongly distorted. $\text{Zr}(1B)$ has five Ir atoms at short distances (slightly shorter) like $\text{Zr}(1)$ while for $\text{Zr}(1A)$ one of these Ir atoms is displaced leaving four Ir atoms at short distances. The coordination polyhedron of the minority-atom site in the Mn_5Si_3 -type structure is generally described as a tricapped trigonal prism. This is true also for the $\text{Ir}(B)$ site, whereas in the case of $\text{Ir}(A)$ one of these nine majority atoms is at a considerably longer distance. It may be noticed that after the combined displacement of $\text{Zr}(2A)$ atoms perpendicular to the c axis and of $\text{Ir}(A)$ atoms more or less parallel to the z direction, the c parameter of the superstructure divided by three is longer than the c parameter measured for the simple Mn_5Si_3 parent type structure, whereas the a parameter is slightly shorter.

One of the reasons for the formation of the superstructure might be that it allows the very strong contraction of the atoms on the $\frac{1}{3}z$ and $\frac{2}{3}z$ axes to be slightly released. As can be expected from this argumentation the Mn_5Si_3 parent type structure has been observed in the $\text{Zr}(\text{or Hf}) - \text{Ir}$ phase diagram only on the $\text{Zr}(\text{Hf})$ -poor side of the stoichiometric composition ($\text{Zr}_{<5}\text{Ir}_3$, $\text{Hf}_{<5}\text{Ir}_3$). However, in the $\text{Zr} - \text{Pt}$ system, Schubert & coworkers (Raman & Schubert, 1964; Biswas & Schubert, 1967) observed at the stoichiometry 5-3 a phase crystallizing with the Mn_5Si_3 parent type, and no indications of a superstructure. The fact that the c parameter of this phase is even shorter than that measured for $\text{Zr}_{<5}\text{Ir}_3$, resulting in yet shorter $\text{Zr} - \text{Zr}$ distances parallel to the c axis, seems to suggest

that this simple explanation of the formation of the superstructure is not sufficient. Another possible reason for the existence of this superstructure could be the reduction of the coordination number of two thirds of the Ir atoms in the structure from nine in the parent structure to eight in the superstructure. The Ir atoms in the neighbouring phases Zr₃Ir (α -V₃S type) and Zr₂Ir (Cu₂Al type) are also surrounded by eight atoms at short distances. In a Zr-deficient Zr_{1₅}Ir₃ structure of Mn₅Si₃ parent type the average coordination number of the Ir atoms would also be less than nine. Furthermore, by focusing the argumentation on the minority atoms it becomes easier to comprehend the difference in behaviour between Zr₅Ir₃ and Zr₅Pt₃. A possible explanation for the existence of Zr₅Pt₃ with the Mn₅Si₃ parent structure, despite the very short Zr–Zr distances, could be the extraordinary stability of the Zr–Pt bond. According to Brewer & Wengert (1973) the Gibbs energy of formation of Zr₅Pt₃, calculated at 1800 K, is about three times larger than that calculated for Zr₅Ir₃.

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Table 2. Interatomic distances (d) up to 4 Å and $\Delta = (d - \sum r) / \sum r$ for Zr₅Ir₃, *hP48*, *P6₁22*, and Zr_{1₅}Ir₃, *hP16*, *P6₃/mcm*

E.s.d.'s are given in parentheses. Atomic radii (r) used for Zr and Ir are 1.602 and 1.357 Å respectively (Teatum *et al.*, 1960).

Zr ₅ Ir ₃ , <i>hP48</i>			Zr _{1<sub>5</sub>} Ir ₃ , <i>hP16</i>					
$a = 7.9306, c = 17.010 \text{ \AA}$			$a = 8.025, c = 5.488 \text{ \AA}$					
Zr(1A)	$d(\text{\AA})$	$\Delta(\%)$	Zr(1B)	$d(\text{\AA})$	$\Delta(\%)$	Zr(1)	$d(\text{\AA})$	$\Delta(\%)$
Ir(B)	2.735 (4)	–7.6	2Ir(A)	2.751 (1)	–7.0	2Ir	2.810	–5.0
Ir(A)	2.865 (4)	–3.2	2Ir(A)	2.755 (3)	–6.9	Ir	2.835	–4.2
Ir(A)	2.872 (5)	–2.9	Ir(B)	2.880 (5)	–2.7	2Ir	3.014	+1.9
Ir(B)	2.988 (3)	+1.0	2Zr(1A)	3.300 (6)	+3.0	4Zr(2)	3.378	+5.4
Zr(2A)	3.166 (5)	–1.2	2Zr(2B)	3.330 (3)	+3.9	4Zr(2)	3.379	+5.5
Zr(1A)	3.262 (4)	+1.8	2Zr(1B)	3.450 (2)	+7.7	2Zr(1)	3.415	+6.6
Zr(2A)	3.275 (3)	+2.2	2Zr(1A)	3.491 (3)	+9.0			
Zr(1A)	3.281 (5)	+2.4	2Zr(2A)	3.806 (3)	+18.8			
Zr(1B)	3.300 (7)	+3.0						
Zr(2B)	3.335 (3)	+4.1						
2Zr(1A)	3.394 (4)	+5.9						
Zr(1B)	3.491 (4)	+9.0						
Zr(2B)	3.534 (5)	+10.3						
Ir(A)	3.581 (3)	+21.0						
Zr(2A)			Zr(2B)			Zr(2)		
2Ir(A)	2.722 (1)	–8.0	2Ir(A)	2.773 (3)	–6.3	2Zr(2)	2.744	–14.4
2Ir(A)	2.897 (2)	–2.1	2Ir(A)	2.800 (1)	–5.4	6Ir	2.807	–5.1
2Zr(2B)	2.899 (1)	–9.5	2Zr(2A)	2.899 (1)	–9.5	6Zr(1)	3.378	+5.4
2Ir(B)	2.948 (2)	–0.4	2Ir(B)	2.937 (2)	–0.7			
2Zr(1A)	3.166 (4)	–1.2	2Zr(1B)	3.330 (4)	+3.9			
2Zr(1A)	3.275 (5)	+2.2	2Zr(1A)	3.335 (3)	+4.1			
2Zr(1B)	3.806 (3)	+18.8	2Zr(1A)	3.534 (3)	+10.3			
Zr(2B)	3.910 (1)	+22.0	Zr(2A)	3.910 (1)	+22.0			
Ir(A)			Ir(B)			Ir		
Zr(2A)	2.722 (2)	–8.0	2Zr(1A)	2.735 (4)	–7.6	4Zr(2)	2.807	–5.1
Zr(1B)	2.751 (6)	–7.0	Zr(1B)	2.880 (5)	–2.7	2Zr(1)	2.810	–5.0
Zr(1B)	2.755 (3)	–6.9	2Zr(2B)	2.937 (2)	–0.7	Zr(1)	2.835	–4.2
Zr(2B)	2.773 (3)	–6.3	2Zr(2A)	2.948 (2)	–0.4	2Zr(1)	3.014	+1.9
Zr(2B)	2.800 (1)	–5.4	2Ir(A)	2.956 (2)	+8.9	2Ir	3.171	+16.8
Zr(1A)	2.865 (3)	–3.2	2Zr(1A)	2.988 (3)	+1.0			
Zr(1A)	2.872 (5)	–2.9						
Zr(2A)	2.897 (2)	–2.1						
Ir(B)	2.956 (2)	+8.9						
Zr(1A)	3.581 (3)	+21.0						
Ir(A)	3.637 (2)	+34.0						
Ir(A)	3.898 (2)	+43.6						

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Structure of the Linear Chain Tetraammineplatinum(II)diidotetraammineplatinum(IV) Hydrogensulfate Dihydrate

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Abstract. $[\text{Pt}(\text{NH}_3)_4][\text{PtI}_2(\text{NH}_3)_4](\text{HSO}_4)_4 \cdot 2\text{H}_2\text{O}$, $M_r = 1204.53$, monoclinic, $C2/m$, $a = 18.609(2)$, $b = 7.563(1)$, $c = 11.862(1)$ Å, $\beta = 126.22(1)^\circ$, $V = 1346.8(6)$ Å³, $Z = 2$, $D_x = 2.97$ Mg m⁻³, D_m not measured, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu(\text{Mo K}\alpha) = 13.61$ mm⁻¹, $F(000) = 1116$, room temperature, $R = 0.041$, $wR = 0.053$ for 1815 observed reflections [$|F_o| > 3\sigma(|F_o|)$]. This compound comprises linear chains $\dots\text{I}-\text{Pt}^{\text{IV}}-\text{I}\dots\text{Pt}^{\text{II}}\dots$ which consist of the alternately arranged octahedral $\text{trans}[\text{PtI}_2(\text{NH}_3)_4]^{2+}$ and square-planar $[\text{Pt}(\text{NH}_3)_4]^{2+}$ units along the c axis. $\text{Pt}^{\text{IV}}-\text{I}$ and $\text{Pt}^{\text{II}}\dots\text{I}$ distances are 2.699(1) and 3.237(1) Å respectively. There is three-dimensional ordering among chains, different from other I-bridged Wolfram's red salt analogues. The difference between the $\text{Pt}^{\text{IV}}-\text{X}$ and $\text{Pt}^{\text{II}}\dots\text{X}$ distances is found to decrease linearly with an increase in the ratio of $\text{Pt}^{\text{IV}}-\text{X}$ to $\text{Pt}^{\text{II}}\dots\text{X}$ distances in Wolfram's red salt analogues, irrespective of the kind of bridging halogen atom X . The data presented in this paper are consistent with this relationship.

Introduction. Since Wolfram's red salt $[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4][\text{PtCl}_2(\text{C}_2\text{H}_5\text{NH}_2)_4]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ was synthesized, many analogues have been synthesized and studied, through substitution of the ligand amines,

bridging halide ions, and counter ions (Endres, Keller, Martin & Traeger, 1979; Matsumoto, Yamashita, Kida & Ueda, 1979; Endres, Keller, Martin, Traeger & Novotny, 1980). They comprise linear chains of halide-bridged platinum ions in the two different oxidation states Pt^{II} and Pt^{IV} and counter anions. These analogues exhibit considerable interactions between platinum ions in each chain through bridging halide ions. The XPS spectral measurement suggests that the oxidation state of Pt is not strictly divalent or tetravalent (Yamashita, Matsumoto & Kida, 1978). A theoretical treatment related to the Peierls state in one-dimensional solids has been carried out by Nasu (1984).

The compounds also show interesting physical properties: a conductivity of 10^{-8} – 10^{-12} Ω⁻¹ cm⁻¹ at room temperature with semiconductive temperature dependence, a strong absorption in the visible region (Yamada & Tsuchida, 1956; Day, 1975; Matsumoto, Yamashita & Kida, 1978; Papavassiliou & Zdetris, 1980), photoluminescence (Tanino & Kobayashi, 1983). The conductivity increases by a factor of 10^3 or more under a pressure of about 10^9 Pa (Thomas & Underhill, 1971; Hamaue, Aoki, Yamashita & Kida, 1981; Aoki, Hamaue, Kida, Yamashita, Takemura, Furuta & Kawamori, 1982).